AD-A036 271 CALIFORNIA UNIV BERKELEY DEPT OF MECHANICAL ENGINEERING F/G 20/13
ON THERMODYNAMICS AND THE NATURE OF THE SECOND LAW: I. SINGLE P--ETC(U)
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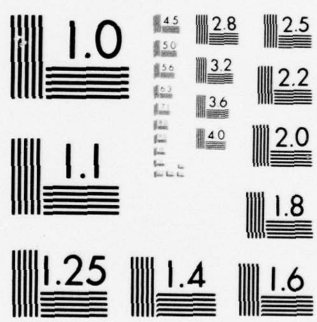

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OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0148

Project NR 064-436

Report No. UCB/AM-76-7

Supplement to Report AM-76-2

"On Thermodynamics and the Nature of the Second Law:

I. Single Phase Continua"

by

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December 1976

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Supplement to

Report AM-76-2

"On Thermodynamics and the Nature of the Second Law: I. Single Phase Continua"

by

A. E. Green[†] and P. M. Naghdi[‡]

Abstract. The contents of this report supplement those of a previous report, namely Report No. AM-76-2, entitled "On thermodynamics and the nature of the second law: I. Single phase continua." In particular, the present supplement contains some additional development concerning the mathematical statement of the second law and restrictions on the heat conduction vector and internal energy, as well as two examples which demonstrate some shortcomings of the Clausius-Duhem inequality. One of the examples, when studied with the use of the Clausius-Duhem inequality, leads to results that imply the possibility of a perpetual motion of the second kind. In the second example, which is concerned with a rigid heat conductor in thermal equilibrium, the Clausius-Duhem inequality requires that if heat is added to the medium the resulting spatially homogeneous temperature of the conductor decreases. Moreover, the inequality denies the possibility of propagation of heat in the conductor as a thermal wave with finite speed. The inequalities proposed here do not suffer from these shortcomings.

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1. Foreword

The contents of this report supplement those of a previous report, namely Report No. AM-76-2 (April 1976), entitled "On thermodynamics and the nature of the second law: I. Single phase continua." In particular, the present Supplement contains (a) some additional development concerning the mathematical statement of the second law and restrictions on the heat conduction vector and internal energy, (b) two specific examples which demonstrate some shortcomings of the Clausius-Duhem inequality and (c) a derivation of jump conditions across a surface of discontinuity from the balance of entropy.*

In order to make this Supplementary Report reasonably self-contained, in the next two sections we collect the basic equations which result from the conservation laws and also provide some general background material from §§2,3 of the previous report (Green and Naghdi 1976). In the present §4, we discuss a revised version of the previous development concerning the second law in a way which considerably enhances the thrust of the main ideas presented in §4 of Green and Naghdi (1976). Also, in the present §5, we recall the previous restriction on the heat conduction vector (see §5 of Green and Naghdi 1976) and then introduce here a further restriction on the internal energy. Next, in §6 we discuss some aspects of the Clausius-Duhem inequality and by means of two specific examples examine the consequences of this inequality and contrast these with the type of restrictions which result from our present thermodynamical developments. Both examples demonstrate the shortcomings of the Clausius-Duhem inequality in certain dissipative media. In fact, one of the examples when studied with the use of the Clausius-Duhem inequality leads to results that imply the possibility of a perpetual motion of the second kind, while the

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*Previously in Report No. AM-76-2, we used the word "calory" in place of "entropy" mainly in order to avoid possible confusion with the latter in the existing literature. However, we now believe that it is best to revert to the more familiar terminology of entropy.

restrictions which emerge from the inequality proposed here deny such a perpetual motion. We close this Supplement by providing a derivation of jump condition across a surface of discontinuity from the balance of entropy in §7. While the derivation of the usual jump conditions from the conservation laws is straightforward and is well understood, the one that can be deduced from the balance of entropy requires special care and this is the main reason for providing the details of the derivation in §7.

2. General background.

Consider a finite body $\mathcal{B}$ with material points X and identify the material point X with its position $\underset{\sim}{X}$ in a fixed reference configuration. A motion of the body is defined by a sufficiently smooth vector function $\underset{\sim}{\chi}$ which assigns position $\underset{\sim}{x} = \underset{\sim}{\chi}(\underset{\sim}{X},t)$ to each material point $\underset{\sim}{X}$ at each instant of time t. In the present configuration at time t, the body $\mathcal{B}$ occupies a region of space $\mathcal{R}$ bounded by a closed surface $\partial\mathcal{R}$. Similarly, in the present configuration, an arbitrary material volume of $\mathcal{B}$ occupies a portion of the region of space $\mathcal{R}$, which we denote by $\mathcal{P}(\subseteq \mathcal{R})$ bounded by a closed surface $\partial\mathcal{P}$.

Let $\rho = \rho(\underset{\sim}{X},t)$ be the mass density in the present configuration and designate the velocity vector at time t by $\underset{\sim}{v} = \dot{\underset{\sim}{x}}$, where a superposed dot denotes material time derivative. Further let $\underset{\sim}{b} = \underset{\sim}{b}(\underset{\sim}{X},t)$ denote the body force per unit mass acting on $\mathcal{B}$ in the present configuration, $\bar{\underset{\sim}{t}}$ be the external surface force per unit area acting on the boundary $\partial\mathcal{R}$, and $\underset{\sim}{t} = \underset{\sim}{t}(\underset{\sim}{X},t\,;\underset{\sim}{n})$ be the internal surface force per unit area acting on $\partial\mathcal{P}$ with $\underset{\sim}{n}$ as its outward unit normal; the field $\underset{\sim}{t}$, called the stress vector, assumes the value $\bar{\underset{\sim}{t}}$ on $\partial\mathcal{R}$. In terms of the above notations and under suitable continuity assumptions, the usual conservation laws for mass, momentum and moment of momentum yield the following local forms:

$$
\begin{gathered}
\dot{\rho} + \rho \operatorname{div} \underset{\sim}{v} = 0 \quad , \\
\operatorname{div} \underset{\sim}{T} + \rho \underset{\sim}{b} = \rho \dot{\underset{\sim}{v}} \quad , \quad \underset{\sim}{t} = \underset{\sim}{T}\underset{\sim}{n} \quad , \qquad (2.1) \\
\underset{\sim}{T}^T = \underset{\sim}{T} \quad ,
\end{gathered}
$$

where $\underset{\sim}{T}$ in $(2.1)_{2,3}$ is the stress tensor, $\underset{\sim}{T}^T$ its transpose and div stands for the divergence operator with respect to the place $\underset{\sim}{x}$ keeping t fixed.

In the interest of clarity and for later reference, we now repeat in some detail from the previous report (Green and Naghdi 1976) the various notations pertaining to the thermal properties of the body and the equations for conservation

of entropy and energy. Thus, we introduce first the absolute temperature at each material point by a scalar field $\theta = \theta(\underset{\sim}{X},t) > 0$. Along with the temperature, we admit the existence of an external rate of supply of heat $r = r(\underset{\sim}{X},t)$ per unit mass, an external rate of surface supply of heat $-\bar{h}$ per unit area acting across $\partial\mathcal{R}$. Also, we assume the existence of an internal surface flux of heat $-h = -h(\underset{\sim}{X},t\,;\underset{\sim}{n})$ per unit area across each surface $\partial\mathcal{P}$; the field h, called the heat flux and measured per unit area per unit time, assumes the value $\bar{h}$ on $\partial\mathcal{R}$. We now define the ratio of the heat supply r to temperature as $s = s(\underset{\sim}{X},t)$ and call this the <u>external rate of supply of entropy</u> per unit mass. Similarly we define the ratios of $\bar{h}$ and h to temperature, respectively, as the <u>external rate of surface supply of entropy</u> $\bar{k}$ per unit area of $\partial\mathcal{R}$ and the <u>internal surface flux of entropy</u> $k = k(\underset{\sim}{X},t\,;\underset{\sim}{n})$ per unit area of $\partial\mathcal{P}$. These definitions may be conveniently summarized by

$$r = \theta s \quad , \quad \bar{h} = \theta\bar{k} \quad , \quad h = \theta k \quad . \tag{2.2}$$

In addition, throughout $\mathcal{R}$ we assume the existence of a scalar field $\eta = \eta(\underset{\sim}{X},t)$ per unit mass, called the <u>specific entropy</u>, and an <u>internal rate of production of entropy</u> $\xi = \xi(\underset{\sim}{X},t)$ per unit mass. The contribution of the latter to the internal rate of production of heat is simply $\theta\xi$ per unit mass.

Although the external rates of volume supply and the external rates of surface supplies of entropy and heat are related by $(2.2)_{1,2}$, we could regard k and h as independent internal fluxes with no a priori connecting relation $(2.2)_3$. Then, instead of $(2.2)_3$, we would have $k = h/\theta + \lambda$ where λ is an independent flux subject to the condition $\lambda = 0$ on $\partial\mathcal{R}$ so that $k = \bar{k}$ on $\partial\mathcal{R}$. For a wide class of simple materials which are homogeneous in a reference configuration, it has been shown by Green and Naghdi (1972) that $\lambda = 0$ everywhere in $\mathcal{R}$ follows from the condition that $\lambda = 0$ on $\partial\mathcal{R}$. Hence, with little loss in generality, we adopt the form $(2.2)_3$ in the present paper.

We now postulate a balance of entropy for every material volume occupying a part $\mathcal{P}$ in the present configuration and write

$$\frac{d}{dt}\int_{\mathcal{P}} \rho\eta\, dv = \int_{\mathcal{P}} \rho(s+\xi)dv - \int_{\partial\mathcal{P}} k\, da \quad . \tag{2.3}$$

By usual procedures, it can be shown from (2.3) that k is linear in $\underset{\sim}{n}$, i.e.,

$$k = \underset{\sim}{p}\cdot\underset{\sim}{n} \quad , \tag{2.4}$$

where $\underset{\sim}{p}$ is called the <u>entropy</u> <u>flux</u> <u>vector</u>. Then, from $(2.2)_3$ and (2.4), $h = \theta\underset{\sim}{p}\cdot\underset{\sim}{n}$ and we may define the heat flux vector $\underset{\sim}{q}$ by

$$\underset{\sim}{q} = \theta\underset{\sim}{p} \quad . \tag{2.5}$$

Under suitable continuity assumptions and with the use of (2.4), the field equation resulting from (2.3) is**

$$\rho\dot{\eta} = \rho(s+\xi) - \operatorname{div}\underset{\sim}{p} \quad . \tag{2.6}$$

At this point we introduce the first law of thermodynamics, known also as the balance of energy, which states that heat and mechanical energy are equivalent and that together they are conserved for every material volume. Thus, with reference to the present configuration, the balance of energy may be stated in the form†

**It is worth recalling here that in the special case of a gas or an inviscid fluid and starting only with the energy equation and appropriate constitutive equations, it can be demonstrated that two scalar functions θ,η exist such that an equation of the form (2.6) holds with s and k given by $(2.2)_{1,3}$ and with $\rho\theta\xi = -\underset{\sim}{p}\cdot\underset{\sim}{g}$, $\underset{\sim}{g}$ being the temperature gradient. This result serves in part as the motivation for the balance equation (2.3) which is applicable to all single phase continua.

†A more primitive form of balance of energy involves an internal rate of production of energy. In order to deny the possibility that the combined thermal and mechanical energy can continually be extracted from the body in closed cycles of deformation and temperature, the internal rate of production of energy is expressed as the time derivative of an internal energy density ϵ. See, in this connection, Green and Naghdi (1971a, p. 42; 1972, p. 356).

$$\frac{d}{dt}\int_{\mathcal{P}}(\tfrac{1}{2}\,\rho\underset{\sim}{v}\cdot\underset{\sim}{v}+\rho\epsilon)dv$$

$$=\int_{\mathcal{P}}(\rho r+\rho\underset{\sim}{b}\cdot\underset{\sim}{v})dv+\int_{\partial\mathcal{P}}(\underset{\sim}{t}\cdot\underset{\sim}{v}-h)da \quad , \tag{2.7}$$

where $\epsilon=\epsilon(\underset{\sim}{X},t)$ is the specific internal energy. With the help of (2.1) and (2.6) and under appropriate continuity assumptions, the field equation resulting from (2.7) is

$$-\rho(\dot{\epsilon}-\theta\dot{\eta})+\underset{\sim}{T}\cdot\underset{\sim}{D}-\rho\xi\theta-\underset{\sim}{p}\cdot\underset{\sim}{g}=0 \quad , \tag{2.8}$$

where $\underset{\sim}{D}$ is the rate of deformation tensor, $\underset{\sim}{p}$ is defined by (2.4), $\underset{\sim}{g}=\operatorname{grad}\theta$ and grad is the gradient operator with respect to $\underset{\sim}{x}$ keeping t fixed. Introducing the specific Helmholtz free energy $\psi=\psi(\underset{\sim}{X},t)$ by

$$\psi=\epsilon-\theta\eta \quad , \tag{2.9}$$

the energy equation (2.8) may be written in the alternative form

$$-\rho(\dot{\psi}+\eta\dot{\theta})+\underset{\sim}{T}\cdot\underset{\sim}{D}-\rho\xi\theta-\underset{\sim}{p}\cdot\underset{\sim}{g}=0 \quad . \tag{2.10}$$

3. Expressions for external mechanical work and external heat supply. Results for elasticity.

For later use, we record here the expressions for the external mechanical work and the external heat supplied to a material volume $\mathcal{P}$ during the time interval $t_1 \leq t \leq t_2$. Guided by known results in elasticity, we first observe that in the case of an elastic material the response functions for ψ, η, ϵ depend only on the deformation gradient $\underset{\sim}{F}$ and the temperature θ and are independent of their rates and the temperature gradient $\underset{\sim}{g}$. Such an elastic material will be regarded as nondissipative in a sense that will be made precise later; and, in conjunction with an expression for the external mechanical work supplied to any part $\mathcal{P}$, will be used as a basis for establishing in §4 an inequality representing the second law of thermodynamics for dissipative materials. Keeping this background in mind, we assume that the constitutive response functions for ϵ, η include also dependence on the set of variables $\dot{F}, \dot{\theta}, \underset{\sim}{g}$ and their higher space and time derivatives and refer to this set collectively as $\mathcal{V}$. Further, let ϵ', η' denote the respective values of ϵ, η when the variables $\mathcal{V}$ are set equal to zero in the response functions.** Thus, for example,

$$
\begin{gathered}
\epsilon = \epsilon(\underset{\sim}{F}, \theta, \mathcal{V}) \quad , \quad \epsilon' = \epsilon'(\underset{\sim}{F}, \theta) = \epsilon(\underset{\sim}{F}, \theta, 0) \quad , \\
\mathcal{V} = (\dot{\underset{\sim}{F}}, \theta, \underset{\sim}{g}, \ldots) \quad ,
\end{gathered}
\tag{3.1}
$$

where the dots in $(3.1)_3$ refer to the higher space and time derivatives of $\dot{\underset{\sim}{F}}, \dot{\theta}, \underset{\sim}{g}$. Then, with the help of (2.1) and the integral of (2.7) with respect to time, we obtain

$\mathcal{W}$ = External mechanical work supplied to a part $\mathcal{P}$ of the body during the time interval $t_1 \leq t \leq t_2$

$$
\begin{aligned}
&= \int_{t_1}^{t_2} \left[\int_{\mathcal{P}} \rho \underset{\sim}{b} \cdot \underset{\sim}{v} \, dv + \int_{\partial \mathcal{P}} \underset{\sim}{t} \cdot \underset{\sim}{v} \, da \right] dt \\
&= \int_{\mathcal{P}} \left(\tfrac{1}{2} \rho \underset{\sim}{v} \cdot \underset{\sim}{v} + \rho \epsilon' \right) dv \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \int_{\mathcal{P}} (-\rho \dot{\theta} \eta' + \rho w) dv \, dt
\end{aligned}
\tag{3.2}
$$

** These definitions of ϵ', η' do not exclude their dependence on the past histories of $\underset{\sim}{F}, \theta, \underset{\sim}{g}$.

and

$\mathcal{H}$ = External heat supplied to a part $\mathcal{P}$ of the body during the time interval $t_1 \leqq t \leqq t_2$

$$= \int_{t_1}^{t_2} [\int_{\mathcal{P}} \rho r \, dv - \int_{\partial\mathcal{P}} h \, da] dt$$

$$= \int_{\mathcal{P}} \rho(\varepsilon - \varepsilon')dv \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \int_{\mathcal{P}} (\rho\theta\dot{\eta}' - \rho w) dv \, dt \quad , \tag{3.3}$$

where

$$\begin{gathered} \rho w = -\rho(\dot{\psi}' + \eta'\dot{\theta}) + \underset{\sim}{T} \cdot \underset{\sim}{D} = \rho[\dot{\psi} - \dot{\psi}' + (\eta - \eta')\dot{\theta}] + \rho\xi\theta + \underset{\sim}{p} \cdot \underset{\sim}{g} \quad , \\ \psi' = \varepsilon' - \theta\eta' \quad . \end{gathered} \tag{3.4}$$

It should be clear that in situations where ε, η do not depend on the set of variables $(3.1)_3$, then $\varepsilon = \varepsilon'$, $\eta = \eta'$, $\psi = \psi'$ and the expressions $(3.3)_3$ and (3.4) simplify considerably.

We now recall the main constitutive results for an elastic material from §3 of the previous report (Green and Naghdi 1976) and also obtain the appropriate expressions for the external mechanical work and external heat supplied to a part $\mathcal{P}$. Thus, by the procedure indicated previously (Green and Naghdi 1976), we require $(2.1)_4$ and (2.10) to be satisfied identically for all processes and this leads to the results

$$\psi = \psi' = \hat{\psi}(\underset{\sim}{C}, \theta ; \underset{\sim}{X}) \quad , \quad \eta = \eta' = -\frac{\partial\hat{\psi}}{\partial\theta} \quad , \quad \underset{\sim}{T} = \rho \underset{\sim}{F} (\frac{\partial\hat{\psi}}{\partial \underset{\sim}{C}} + \frac{\partial\hat{\psi}}{\partial \underset{\sim}{C}^T}) \underset{\sim}{F}^T \quad , \tag{3.5}$$

$$\rho\xi\theta = -\underset{\sim}{p} \cdot \underset{\sim}{g} \quad , \tag{3.6}$$

where $\hat{\psi}$ is the Helmholtz free energy response function and

$$\underset{\sim}{C} = \underset{\sim}{F}^T \underset{\sim}{F} \tag{3.7}$$

is the Cauchy-Green measure of deformation. With the use of (3.6) and (2.5), (2.6) reduces to

$$\rho r - \operatorname{div} \underset{\sim}{q} = \rho\theta\dot{\eta} \quad . \tag{3.8}$$

With the help of (3.5), (3.6) and (3.2) to (3.4), we record below for an elastic material the expressions representing (i) work by body and surface forces on any part $\mathcal{P}$ and (ii) supply of energy arising from the rate of supply of heat and the surface flux of heat to $\mathcal{P}$, both over a finite time interval $(t_1 \leq t \leq t_2)$:

$$\begin{aligned} \mathcal{W} &= \int_{t_1}^{t_2} [\int_{\mathcal{P}} \rho \underset{\sim}{b} \cdot \underset{\sim}{v}\, dv + \int_{\partial\mathcal{P}} \underset{\sim}{t} \cdot \underset{\sim}{v}\, da] dt \\ &= \int_{\mathcal{P}} \rho(\tfrac{1}{2}\, \underset{\sim}{v} \cdot \underset{\sim}{v} + \varepsilon')dv \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \int_{\mathcal{P}} \rho\theta\dot{\eta}' dv\, dt \\ &= \int_{\mathcal{P}} \rho(\tfrac{1}{2}\, \underset{\sim}{v} \cdot \underset{\sim}{v} + \psi')dv \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \int_{\mathcal{P}} \rho\eta'\dot{\theta}\, dv\, dt \end{aligned} \tag{3.9}$$

and

$$\mathcal{H} = \int_{t_1}^{t_2} [\int_{\mathcal{P}} \rho r\, dv - \int_{\partial\mathcal{P}} \underset{\sim}{q} \cdot \underset{\sim}{n}\, da] dt = \int_{t_1}^{t_2} \int_{\mathcal{P}} \rho\theta\dot{\eta}' dv\, dt \quad . \tag{3.10}$$

Since ε' and η' are functions of θ and $\underset{\sim}{C}$, it follows from (3.9) that the work done on the body in any process -- represented by any path in the seven-dimensional space of temperature θ and deformation measure $\underset{\sim}{C}$ -- may be completely recovered by reversing the path and returning to the initial values of $\theta, \underset{\sim}{C}$ and $\underset{\sim}{v}$. A similar result holds for the heat supplied to the body. The external work supplied to any part $\mathcal{P}$ of an elastic body is given by (3.9) and we make use of this fact in §4.

In the next two sections we discuss the second law of thermodynamics, as well as restrictions on the heat conduction vector and the internal energy. Although the contents of these two sections include some modifications of and additions to the corresponding previous developments (§§4,5 of Green and Naghdi 1976), a good deal of the present §§4,5 overlap with the corresponding previous developments in order to render this Supplement reasonably self-contained.

4. The second law of thermodynamics.

In the first law it is assumed that mechanical energy can be changed into heat energy and conversely, and no restriction is placed on the transformation of one into the other. It appears to be a fact of experience that whereas the transformation of mechanical energy into heat, for example through friction, is not limited by any restrictions, the reverse process, namely the transformation of heat into mechanical energy, is subject to definite limitations. This fact has been incorporated into a number of different statements which are then usually called the second law of thermodynamics. It is often asserted that the various statements of the second law are equivalent although proofs of these are far from convincing and usually limited to special situations. For example a form of second law attributed to Kelvin (1851) is*:

(A) It is impossible to construct an engine which would extract heat from a given source and transform it into mechanical energy, without bringing about some additional changes in the bodies taking part. A slight variant of this statement which involves periodic cycles is due to Planck and is known as the Kelvin-Planck statement of the second law.

Another form of the second law is:

(B) It is impossible completely to reverse a process in which energy is transformed into heat by friction.

There are other statements of similar character such as that due to Carathéodory. A somewhat different idea seems to be involved in the form of second law attributed to Clausius (1850):

(C) Heat cannot pass spontaneously from a body of lower temperature to a body of higher temperature.

*The various versions of the second law are recalled here as statements (A), (B) and (C). These or variants thereof can be found in standard books on thermodynamics, e.g., Schmidt (1949), Zemansky (1968), Pippard (1966) and ter Haar and Wergeland (1966).

A statement such as (C) does not necessarily involve the concept of mechanical work since it could be applied to rigid heat conducting solids but many books contain "proofs" that (C) is equivalent to (A) or (B).

Although the first two of the above statement convey the idea that some restrictions must be placed on the interchangeability of energy due to heat and mechanical work, they are not precise. Attempts to make this notion precise in the context of single phase continuum mechanics have led to controversy, although there is a measure of agreement about many of the results which emerge from the restrictions. Most trouble seems to center on the concept of entropy, even though none of the above statements appear to involve entropy. In recent years it has become customary for some workers in continuum mechanics to postulate the existence of a scalar function called entropy and an entropy inequality called the Clausius-Duhem inequality. With the help of this inequality restrictions are placed on constitutive equations, and some of these restrictions do seem to embody concepts contained in statements such as (A), (B) or (C). However, at the outset, it is not at all clear how the ideas contained in (A), (B) or (C) have been translated into the Clausius-Duhem inequality. Some writers have raised objections to this inequality for other reasons but it is not our purpose to discuss these objections here.

In the present section, we reconsider a mathematical interpretation of some form of second law of thermodynamics for single phase continua and adopt a statement of this law which is similar to that of the statement (B) above. First we observe that the expression $(3.2)_2$, when evaluated for a given process, may be either positive or negative depending on whether the external work is supplied to or withdrawn from $\mathcal{P}$. This external work is also represented by $(3.2)_3$ in terms of both thermal and mechanical variables but not every term in $(3.2)_3$ need necessarily be positive (zero or negative), even though the external work may be positive (zero or negative). Thus, with reference to a dissipative material,

we assume that in every admissible process a part of external work is always converted into heat which cannot be withdrawn from $\mathcal{P}$ as mechanical work and is therefore nonnegative. This means that the external work can be expressed as the sum of two parts, one of which is nonnegative and the other, depending on the process, could be positive, zero or negative. Hence, we write

$$\mathfrak{w} = \mathfrak{w}_1 + \mathfrak{w}_2 \quad , \quad \mathfrak{w}_2 \geqq 0 \quad .$$

The above also implies that

$$\mathfrak{w} \geqq \mathfrak{w}_1$$

and $\mathfrak{w}$ is bounded below, the bound depending on the process.

In order to identify the two parts $\mathfrak{w}_1$ and $\mathfrak{w}_2$, we note from (3.5), (3.6) and (3.4) that in the case of an elastic material $w = 0$ in (3.2) and the expression for the external work supplied to $\mathcal{P}$ reduces to (3.9). We now regard an elastic material as being nondissipative in the sense that no restriction is placed on the external mechanical work (3.9) supplied to $\mathcal{P}$ and identify $\mathfrak{w}_1$ with the right-hand side of $(3.2)_3$ after setting $w = 0$. Keeping this in mind, we rewrite the last inequality as

$$\mathfrak{w} \geqq \int_{\mathcal{P}} (\tfrac{1}{2}\, \rho \underset{\sim}{v} \cdot \underset{\sim}{v} + \rho\varepsilon') \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \int_{\mathcal{P}} \rho\theta\dot{\eta}'\, dv\, dt \tag{4.1}$$

and assume that (4.1) holds for every thermo-mechanical process. The combination of (3.2) and the assumption (4.1) yields

$$\int_{t_1}^{t} \int_{\mathcal{P}} \rho w\, dv\, dt \geqq 0 \tag{4.2}$$

for each part $\mathcal{P}$ of $\mathcal{R}$ and for all times t_1, t_2. Since t_1, t_2 are arbitrary and ρw has already been assumed to be continuous, it follows that

$$\int_{\mathcal{P}} \rho w\, dv \geqq 0 \tag{4.3}$$

for all arbitrary $\mathcal{P}$. Hence,

$$\rho w = -\rho(\dot{\psi}' + \eta'\dot{\theta}) + \underset{\sim}{T} \cdot \underset{\sim}{D} \geqq 0 \tag{4.4}$$

for all thermo-mechanical processes. Also, from (3.3) and (4.4), we have

$$\mathcal{H} \leqq \int_{\mathcal{P}} \rho(\epsilon-\epsilon')dv \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2}\int_{\mathcal{P}} \rho\theta\dot{\eta}'\, dv\, dt \tag{4.5}$$

so that the external heat supplied to a part $\mathcal{P}$ of the body is bounded above in every process. Alternatively, some of the heat supplied to the body in every process is always nonpositive. This form of the law is related to the statement (A) above. It should also be noted that the inequality (4.4) is not the same as the Clausius-Planck inequality. However, in the special case for which ψ,η are independent of the set of variables $(3.1)_3$ so that $\psi=\psi'$, $\eta=\eta'$, $\epsilon=\epsilon'$, then (4.4) does reduce to the inequality known as the Clausius-Planck; see, in this connection, Day (1972, p. 49).

The right-hand side of the inequality (4.1) can be expressed in terms of ψ' defined by $(3.4)_3$. We consider a special case of this inequality appropriate for a closed cycle of isothermal process in which θ is constant and the velocity $\underset{\sim}{v}$ assumes the same value, respectively, at the beginning and end of the process. Then,[†]

$$\oint \Big[\int_{\mathcal{P}} \rho\underset{\sim}{b}\cdot\underset{\sim}{v}\, dv + \int_{\partial\mathcal{P}} \underset{\sim}{t}\cdot\underset{\sim}{v}\, da\Big]dt \geqq \int_{\mathcal{P}} \rho\psi' dv \Big|_{t_1}^{t_2} \quad . \tag{4.6}$$

A result similar to (4.6) follows from (4.1) for processes which take place at constant values of η' and spatially homogeneous θ with the velocity $\underset{\sim}{v}$ assuming the same value, respectively, at the beginning and end of the process, provided ψ' in (4.6) is replaced by ϵ'.

We now turn to one other consequence of the inequality (4.4). Suppose $H(t)$ is the total rate at which external heat is supplied to a part $\mathcal{P}$. Then, from (3.3) and (4.33) we have

$$\dot{\mathcal{H}}(t) = H(t) \leqq \dot{\mathcal{E}}(t) - \dot{\mathcal{E}}'(t) + \int_{\mathcal{P}} \rho\theta\dot{\eta}' dv \quad , \tag{4.7}$$

where the expression for $\mathcal{H}(t)$ is given by (2.33) but with t_2 replaced with t and where

$$\mathcal{E}(t) = \int_{\mathcal{P}} \rho\epsilon\, dv \quad , \quad \mathcal{E}'(t) = \int_{\mathcal{P}} \rho\epsilon'\, dv \quad . \tag{4.8}$$

[†]It may be noted that a work inequality of the type employed recently by Naghdi and Trapp (1975a) in the context of the purely mechanical theory is, in general, a separate statement from (4.6). The former work inequality was stated in the reference state and for processes which are closed spatially homogeneous cycles of deformation.

When the temperature is spatially homogeneous so that $\theta = \theta(t)$, it follows from (4.7) that in the time interval $t_1 \leqq t \leqq t_2$ (since $\theta = \theta(t) > 0$)

$$\int_{t_1}^{t_2} \{H(t) - \dot{\mathcal{E}}(t) + \dot{\mathcal{E}}'(t)\} \frac{dt}{\theta(t)} \leqq S'(t_2) - S'(t_1) \quad , \tag{4.9}$$

where

$$S' = \int_{\mathcal{P}} \rho \eta \, dv \quad . \tag{4.10}$$

Moreover, in any closed cycle during the closed interval $[t_1, t_2]$ in which S' has the same value at $t = t_1$ and $t = t_2$, (4.9) becomes

$$\int_{t_1}^{t_2} \{H(t) - \dot{\mathcal{E}}(t) + \dot{\mathcal{E}}'(t)\} \frac{dt}{\theta(t)} \leqq 0 \quad . \tag{4.11}$$

For all continua in which ϵ does not depend explicitly on the set of variables $(3.1)_3$, $\epsilon = \epsilon'$ and $\mathcal{E} = \mathcal{E}'$ by (4.8). Then, (4.11) reduces to

$$\int_{t_1}^{t_2} \frac{H(t)}{\theta(t)} \, dt \leqq 0 \quad . \tag{4.12}$$

The inequality (4.12), derived here only for spatially homogeneous temperature fields, is often called the Clausius inequality. It may be noted also that when the material response is such that $\mathcal{E} = \mathcal{E}'$, then (4.9) reduces to a statement of the Clausius-Planck inequality for spatially homogeneous temperature fields.

5. Restrictions on heat conduction vector and internal energy.

So far we have discussed the second law of thermodynamics from the point of view of interchangeability of heat and mechanical work. This has not yielded any restriction on the form of the heat conduction vector, as can be seen by the special example of an elastic solid in §3. Here we return to the statement (C) in §4 and consider only the heat flux response in equilibrium cases for which heat flow is steady. By equilibrium we mean that

$$\underset{\sim}{v} = \underset{\sim}{0} \quad , \quad \dot{\underset{\sim}{F}} = \underset{\sim}{0} \quad , \quad \dot{\theta} = 0 \text{ for all } t \quad , \tag{5.1}$$

where $\underset{\sim}{F}$ and θ, as well as all other relevant functions, are independent of t (but may depend on $\underset{\sim}{x}$). Then, it follows from (2.6) and (2.8) that

$$\rho\xi\theta = -\underset{\sim}{p} \cdot \underset{\sim}{g} \quad , \quad \rho(s+\xi) = \operatorname{div} \underset{\sim}{p} \quad , \tag{5.2}$$

or

$$\rho r = \rho s\theta = \operatorname{div}(\underset{\sim}{p}\theta) = \operatorname{div} \underset{\sim}{q} \quad . \tag{5.3}$$

For the equilibrium cases under discussion, we adopt the classical heat conduction inequality

$$-\underset{\sim}{q} \cdot \underset{\sim}{g} \geqq 0 \tag{5.4}$$

for all time-independent temperature fields. We recall that when $\underset{\sim}{q}$ is parallel to the temperature gradient $\underset{\sim}{g}$, (5.4) implies that heat flows in the direction of decreasing temperature. In order to relate (5.4) more generally to the statement (C) in §4 we suppose that the external supply of heat is zero so that the right-hand side of (5.3) vanishes also, i.e.,

$$s = r = 0 \quad , \quad \operatorname{div} \mathbf{q} = 0 \quad . \tag{5.5}$$

Further, let a part $\partial\mathcal{R}_1$ of the boundary $\partial\mathcal{R}$ be maintained at constant temperature θ_1 and a part $\partial\mathcal{R}_2$ of $\partial\mathcal{R}$ be maintained at constant temperature θ_2, and that no flow of heat take place across the rest of the boundary $\partial\mathcal{R} - \partial\mathcal{R}_1 - \partial\mathcal{R}_2$. Summarizing these we have

$$\begin{gathered} \theta = \theta_1 \quad \text{on} \quad \partial\mathcal{R}_1 \quad , \quad \theta = \theta_2 \quad \text{on} \quad \partial\mathcal{R}_2 \quad , \\ \mathbf{q} \cdot \mathbf{n} = 0 \quad \text{on} \quad \partial\mathcal{R} - \partial\mathcal{R}_1 - \partial\mathcal{R}_2 \quad . \end{gathered} \tag{5.6}$$

By $(5.5)_2$ and (5.6), we have

$$\int_{\partial\mathcal{R}_1} \mathbf{q} \cdot \mathbf{n} \, da + \int_{\partial\mathcal{R}_2} \mathbf{q} \cdot \mathbf{n} \, da = 0 \quad . \tag{5.7}$$

If we assume that heat flows into the body across $\partial\mathcal{R}_1$ and out of the body across $\partial\mathcal{R}_2$, then

$$\int_{\partial\mathcal{R}_2} \mathbf{q} \cdot \mathbf{n} \, da \geqq 0 \quad . \tag{5.8}$$

Also, we need the result

$$(\theta_1 - \theta_2) \int_{\partial\mathcal{R}_2} \mathbf{q} \cdot \mathbf{n} \, da = - \int_{\partial\mathcal{R}} \theta \mathbf{q} \cdot \mathbf{n} \, da = - \int_{\mathcal{R}} \mathbf{q} \cdot \mathbf{g} \, dv \quad , \tag{5.9}$$

the truth of which can be verified with the help of (5.5), (5.6) and (5.7).

Since (5.4) is assumed to hold for all time-independent temperature fields, it follows from (5.4), (5.8) and (5.9) that

$$\theta_1 \geqq \theta_2 \quad , \tag{5.10}$$

i.e., according to (5.9) and (5.10), heat flows from the higher to the lower temperature in the body. We observe that the result (5.10) would still follow

if we replace (5.4) by

$$-\int_{R} \underset{\sim}{q} \cdot \underset{\sim}{g} \, dv \geqq 0 \tag{5.11}$$

for all time-independent temperature fields.

The condition (5.4) or (5.11), which hold in equilibrium cases, will be utilized in the rest of the paper to impose restrictions on the constitutive equation for the heat flux vector. For many materials of interest, the thermo-mechanical response of the medium is characterized in terms of certain kinematic and thermal variables (such as $\underset{\sim}{F}$ and θ) and their gradients but not their rates. In such cases, once the heat flux response function has been restricted by either (5.4) or (5.11), the resulting conditions remain valid for all values of kinematic and thermal variables and not just the time-independent ones. For example, with reference to the elastic material discussed in §3, the constitutive equation for the heat conduction vector has the form

$$\underset{\sim}{q} = \hat{\underset{\sim}{q}}(\underset{\sim}{F},\theta,\underset{\sim}{g}) \quad , \tag{5.12}$$

and by (5.4) the response function $\hat{\underset{\sim}{q}}$ is restricted by

$$-\hat{\underset{\sim}{q}}(\underset{\sim}{F},\theta,\underset{\sim}{g}) \cdot \underset{\sim}{g} \geqq 0 \tag{5.13}$$

for all arbitrary time-independent values of its arguments. It follows that the condition (5.13) must hold even if $\underset{\sim}{F},\theta,\underset{\sim}{g}$ are functions of both $\underset{\sim}{X}$ and t.

Finally we suppose that the continuum is at rest with $\underset{\sim}{v} = \underset{\sim}{0}$ for all time and with the deformation gradient $\underset{\sim}{F}$ everywhere constant for all time. Then, $\underset{\sim}{D} = \underset{\sim}{0}$ everywhere and it follows from $(2.1)_1$ that ρ is independent of t. In addition, we restrict the temperature field to be spatially homogeneous so that $\theta = \theta(t)$. Keeping these in mind, from combination of (2.6) and (2.8) we have

$$\rho r - \operatorname{div} \underset{\sim}{q} = \rho\dot{\varepsilon} \quad . \tag{5.14}$$

Since $\underset{\sim}{v} = \underset{\sim}{0}$ everywhere no mechanical work is supplied to the body. Then, using (5.14), the heat supplied to a part $\mathcal{P}$ of the body during the time interval $t_1 \leqq t \leqq t_2$ is

$$\mathcal{H} = \int_{t_1}^{t_2} \left[\int_{\mathcal{P}} \rho r \, dv - \int_{\partial \mathcal{P}} \underset{\sim}{q} \cdot \underset{\sim}{n} \, da \right] dt = \int_{\mathcal{P}} \rho \varepsilon \, dv \Big|_{t_1}^{t_2} \quad . \tag{5.15}$$

Now suppose that the body has been in a state of thermal equilibrium during some period up to the time t_1 with constant internal energy ε_1 and constant temperature θ_1. Then, recalling again the statement (C) in §4, we assume that whenever heat is supplied to a part $\mathcal{P}$ according to (5.15), the temperature $\theta(t)$ throughout the part will be increased, i.e.,

$$[\theta]_{t_1}^{t_2} > 0 \quad \text{whenever} \quad \mathcal{H} > 0 \quad . \tag{5.16}$$

Assuming now that $\rho\varepsilon$ is continuous and remembering that ρ is positive and independent of t and $\mathcal{P}$ is arbitrary, it follows from (5.15) and (5.16) that

$$\theta(t) - \theta_1 > 0 \quad \text{whenever} \quad \varepsilon(t) - \varepsilon_1 > 0 \tag{5.17}$$

for all $t > t_1$.

6. A comparison with the Clausius-Duhem inequality.

In this section, we consider the Clausius-Duhem inequality and also by means of two specific examples examine the consequences of this inequality and contrast these with the type of restrictions which result from the present thermodynamical restrictions proposed in §§4,5. Both examples demonstrate the shortcomings of the Clausius-Duhem inequality in certain dissipative media. In fact, one of the examples when studied with the use of the Clausius-Duhem inequality leads to results that imply the possiblity of a perpetual motion of the second kind, while the restrictions which emerge from the inequality proposed here deny such a perpetual motion.

We recall that much of the development in continuum thermomechanics in recent years has been based on the conservation equations for mass, momentum, moment of momentum and energy, where the field equation corresponding to (2.7) is not an identity for all thermo-mechanical processes. Restrictions on constitutive equations are then obtained with the help of the Clausius-Duhem inequality, namely

$$\frac{d}{dt}\int_{\mathcal{P}} \rho\eta\, dv - \int_{\mathcal{P}} \frac{\rho r}{\theta}\, dv + \int_{\partial\mathcal{P}} \frac{\underset{\sim}{q}\cdot\underset{\sim}{n}}{\theta}\, da \geqq 0 \quad , \tag{6.1}$$

where the temperature θ (>0) and entropy η appear for the first time. If we identify θ and η in (6.1) with the corresponding quantities defined in §2, then under suitable continuity assumptions the inequality (6.1) yields

$$\rho\theta\xi = -\rho(\dot{\psi} + \eta\dot{\theta}) + \underset{\sim}{T}\cdot\underset{\sim}{D} - \underset{\sim}{p}\cdot\underset{\sim}{g} \geqq 0 \tag{6.2}$$

for all thermo-mechanical processes.

The above inequality should be contrasted with the inequality (4.4). For materials whose thermo-mechanical response is such that ψ,η are independent of the set of variables $(3.1)_3$, the Helmholtz free energy and the entropy reduce to[§] $\psi = \psi'$, $\eta = \eta'$; and then, after recalling the expression for w in (3.4), the

[§]It may be noted that the cases in which $\psi = \psi'$, $\eta = \eta'$ include a fairly large class of materials of interest.

Clausius-Duhem inequality becomes

$$\rho\theta\xi = \rho w - \underset{\sim}{p}\cdot\underset{\sim}{g} \geqq 0 \quad . \tag{6.3}$$

If $\psi,\eta,\underset{\sim}{T}$, and hence w, do not depend explicitly on the temperature gradient $\underset{\sim}{g}$ and its history, then it readily follows from (6.3) that $\rho w \geqq 0$ which is the same as our inequality (4.4). Further, if it were true that $\underset{\sim}{p}\cdot\underset{\sim}{g} \geqq 0$ (and hence $\underset{\sim}{q}\cdot\underset{\sim}{g} \geqq 0$) for <u>all</u> thermo-mechanical processes, then (6.3) again yields $\rho w \geqq 0$. However, the Clausius-Duhem inequality itself denies this possibility: for equilibrium processes $w = 0$ by $(3.4)_1$ and (6.3) then implies that $\underset{\sim}{p}\cdot\underset{\sim}{g} \leqq 0$. Apart from these observations, it is clear that provided $\underset{\sim}{p}\cdot\underset{\sim}{g} < 0$, the Clausius-Duhem inequality (6.3) could allow ρw to be negative for some materials undergoing particular admissible processes. But a result of this kind does not, in turn, rule out the possibility of a response in a dissipative material which permits a perpetual motion of the second kind. Indeed, we construct below an example and demonstrate the existence of a thermo-mechanical process which, when subjected to restrictions demanded by the Clausius-Duhem inequality, gives rise to a cyclic motion for a dissipative material in which heat is continually supplied to the whole body and continually withdrawn as work so that the efficiency of the process over each cycle is unity.† We also discuss a second example of a different type and demonstrate still other differences which emerge when the Clausius-Duhem inequality (6.3) is employed instead of the inequality (4.4) of the present paper.

Let us suppose that the set of variables $\{\underset{\sim}{T},\psi,\eta,\xi,\underset{\sim}{p}\}$ are functions of the set $\{\theta,\rho,\underset{\sim}{g},\underset{\sim}{L}\}$, where $\underset{\sim}{L}$ is the velocity gradient. Then, either by the method of the present paper or by the use of the Clausius-Duhem inequality, it can be shown that ψ,η,ϵ are, in fact, independent of $\underset{\sim}{L},\underset{\sim}{g}$ and reduce to functions of ρ,θ only; they also coincide with ψ',η',ϵ', respectively. Moreover, invariance under superposed rigid body motions demands that the stress tensor $\underset{\sim}{T}$ and the heat conduction

†A similar cyclic motion was examined for a different purpose previously (Green and Naghdi 1971), where it was demonstrated that Cauchy elasticity is not admissible within the ordinary framework of thermomechanics with an energy equation of the form (2.7).

vector $\underset{\sim}{q}$ be isotropic functions of $\rho, \theta, \underset{\sim}{D}, \underset{\sim}{g}$. From this class of viscous materials, we choose a particular set of constitutive equations in the discussion of our first example.

Example 1. Consider an incompressible viscous fluid characterized by the following constitutive equations:

$$\psi' = \psi = c(\theta - \theta \log \theta) \quad , \quad \eta' = \eta = c \log \theta \quad , \quad \epsilon' = \epsilon = c\theta \quad ,$$

$$\underset{\sim}{T} = -p\underset{\sim}{I} + \underset{\sim}{T}_e \quad , \quad \underset{\sim}{T}_e = \rho(2\mu\underset{\sim}{D} - \alpha \underset{\sim}{D}\underset{\sim}{g}\underset{\sim}{g}) \quad , \tag{6.4}$$

$$\underset{\sim}{q} = -\kappa\underset{\sim}{g} - \rho\beta\theta\underset{\sim}{D}^2\underset{\sim}{g} \quad ,$$

where $c, \rho, \mu, \alpha, \kappa, \beta$ are constants and p is an arbitrary function of $\underset{\sim}{x}$ and t. The Clausius-Duhem inequality (6.2) is satisfied identically if

$$\mu \geqq 0 \quad , \quad \kappa \geqq 0 \quad , \quad \beta \geqq \alpha \quad . \tag{6.5}$$

The constant α is chosen so that $\alpha > 0$. Consider now the homogeneous non-isothermal deformation specified by

$$x_1 = X_1 \exp\{B(1 - \cos \omega t)\} \quad , \quad x_2 = X_2 \exp\{-B(1 - \cos \omega t)\} \quad , \quad x_3 = X_3 \quad ,$$
$$\theta = \theta_o + Ax_1(2 + \sin \omega t) \quad . \tag{6.6}$$

In (6.6), the coefficients A, B are constants (but not necessarily positive), θ_o and ω are positive constants and the value of θ_o is taken to be large enough so that θ is always positive. The corresponding velocity, temperature gradient and rate of deformation tensor at time t are

$$\underset{\sim}{v} = B\omega(x_1\underset{\sim}{e}_1 - x_2\underset{\sim}{e}_2)\sin \omega t \quad , \quad \underset{\sim}{g} = A\underset{\sim}{e}_1(2 + \sin \omega t) \quad ,$$
$$\underset{\sim}{D} = B\omega\{\underset{\sim}{e}_1 \otimes \underset{\sim}{e}_1 - \underset{\sim}{e}_2 \otimes \underset{\sim}{e}_2\}\sin \omega t \quad , \quad \mathrm{tr}\, \underset{\sim}{D} = 0 \quad . \tag{6.7}$$

The motion $(6.6)_{1,2,3}$ and the temperature distribution $(6.6)_4$ are very smooth. They have continuous derivatives of all orders with respect to X_i and t.

Moreover, (6.6) and all their derivatives return to their same values after each interval of time $2\pi/\omega$, as do all the functions in (6.7) and (6.4). Let the body occupy a region $\mathfrak{R}_0$ in its reference configuration at time $t = 0$ and let $H(t)$ be the total rate at which external heat is supplied to the whole body at time t. Then, with the help of (3.3), (3.4) and (6.4) to (6.7), we have

$$
\begin{aligned}
H(t) &= \int_{\mathfrak{R}} \rho r \, dv - \int_{\partial\mathfrak{R}} \underset{\sim}{q} \cdot \underset{\sim}{n} \, da = \int_{\mathfrak{R}} (\rho\theta\dot{\eta}' - \underset{\sim}{T}_e \cdot \underset{\sim}{D}) dv = \int_{\mathfrak{R}_0} (\rho\theta\dot{\eta}' - \underset{\sim}{T}_e \cdot \underset{\sim}{D}) dV \\
&= MB^2\omega^2[\alpha A^2(2 + \sin \omega t)^2 - 4\mu]\sin^2 \omega t \quad ,
\end{aligned} \tag{6.8}
$$

where M is the mass of the body and where we have chosen the origin of the X_i axes to be at the center of mass of the body in its reference configuration. We now choose α to satisfy the inequality

$$\alpha A^2 > 4\mu \geqq 0 \tag{6.9}$$

so that the expression (6.8) for $H(t)$ is always nonnegative for all time. The total heat <u>supplied</u> to the whole body in the time interval $0 \leqq t \leqq 2\pi/\omega$ is then given by

$$\mathcal{H} = \int_0^{2\pi/\omega} H(t) dt = \pi MB^2\omega[4(\alpha A^2 - \mu) + \frac{3}{4} \alpha A^2] \tag{6.10}$$

and during this interval no heat is emitted. Moreover, from (3.2) and (6.4) to (6.7) we see that the total external mechanical work <u>extracted</u> from the whole body during the same time interval is

$$-\mathfrak{w} = \pi MB^2\omega[4(\alpha A^2 - \mu) + \frac{3}{4} \alpha A^2 2 \quad . \tag{6.11}$$

This process can be continued for an indefinite number of cycles and implies a motion in which the efficiency of the process, namely $-\mathfrak{w}/\mathcal{H}$ is equal to unity (since $-\mathfrak{w} = \mathcal{H} > 0$). This corresponds to a perpetual motion of the second kind, since it does not violate the energy equation. To avoid ambiguity, it seems

desirable to provide here a definition for perpetual motion of the second kind with particular reference to the type of medium considered in Example 1: Consider an incompressible viscous fluid, which is characterized by the set of constitutive equations (6.4). We say a fluid of this kind gives rise to a perpetual motion of the second kind if there are periodic motions and temperature fields of period τ such that (i) $\dot{\underset{\sim}{x}}(\underset{\sim}{X},0) = \dot{\underset{\sim}{x}}(\underset{\sim}{X},\tau) = \underset{\sim}{0}$; (ii) $\epsilon(\underset{\sim}{X},0) = \epsilon(\underset{\sim}{X},\tau)$; (iii) the rate of supply of external heat to the whole body and the rate at which work (minus the change in kinetic energy) is withdrawn from the whole body are both positive at each instant of time, and consequently the total heat $\mathfrak{H}$ supplied to the whole body and the total work $-\mathfrak{w}$ withdrawn from the whole body during a period are both positive; and (iv) no heat is emitted from the whole body during the motion so that the ratio $-\mathfrak{w}/\mathfrak{H} = 1$.

In contrast to the implication of the Clausius-Duhem inequality employed in the above discussion, suppose we adopt the inequality (4.4) of the present paper. Then $\alpha \leqq 0$ and no restriction is placed on the coefficient β which occurs in the expression for $\underset{\sim}{q}$. It follows from (6.8), (6.9) and (6.10) that

$$H(t) \leqq 0 \quad , \quad \mathfrak{H} \leqq 0 \quad , \quad \mathfrak{w} \geqq 0 \quad , \tag{6.12}$$

i.e., work is done on the body and is continually withdrawn as heat. Clearly, the use of the inequality (4.4) in the above example does not lead to a perpetual motion.

The second example that we wish to consider is of somewhat different character and is concerned with heat conduction in a fixed homogeneous isotropic rigid solid. It is well known that the classical theory of heat conduction does not allow heat to be propagated with a finite wave speed. Among the many attempts to provide a heat conduction theory in which heat can propagate with a finite wave speed, we mention the one by Bogy and Naghdi (1970) who suggested that $\dot{\theta}$ be added to the list of independent variables in the constitutive equations. They made use of the Clausius-Duhem inequality to

place restrictions on the constitutive response functions and also showed that for a theory which is linearized about a constant equilibrium temperature, heat not only could not propagate with a finite wave speed but its propagation was governed by an elliptic differential equation. We illustrate this here with a simple example and contrast the results with those which follow from our present inequality (4.4).

Example 2. The conduction of heat in a fixed homogeneous isotropic rigid solid may be characterized by the constitutive equations

$$\begin{aligned} \psi &= c\theta(1 - \log \theta) \quad , \quad \eta = c \log \theta - \alpha\dot{\theta}/\theta \quad , \\ \epsilon &= c\theta - \alpha\dot{\theta} \quad , \quad \underset{\sim}{q} = - \kappa \underset{\sim}{g} \quad , \end{aligned} \tag{6.13}$$

where c, α, κ are constants and $\alpha \neq 0$. The Clausius-Duhem inequality (6.2) is then identically satisfied provided

$$\alpha > 0 \quad , \quad \kappa \geqq 0 \tag{6.14}$$

and the energy or the heat conduction equation becomes

$$\rho r + \kappa \nabla^2 \theta = \rho(c\dot{\theta} - \alpha\ddot{\theta}) \quad , \tag{6.15}$$

where ∇^2 is the Laplacian operator. In view of (6.14), the differential equation (6.15) is elliptic and does not allow heat to be propagated as a wave. Moreover, suppose that the solid is in thermal equilibrium prior to the time t_1 with $\theta = \theta_1$ and $\epsilon = c\theta_1$. Then, if heat is continually supplied to every part of the solid when $t > t_1$, it follows from (5.15) and (6.13) that

$$c\theta - \alpha\dot{\theta} > c\theta_1 \quad . \tag{6.16}$$

With the help of the positive integrating factor $\exp(-ct/\alpha)$, integration of the above inequality between the limits t_1 and t yields

$$-\alpha(\theta-\theta_1)\exp(-ct/\alpha) > 0 \quad \text{or} \quad -\alpha(\theta-\theta_1) > 0 \quad . \tag{6.17}$$

But $\alpha > 0$ by $(6.14)_1$ and the last result implies that if heat is continually supplied to the solid, then its temperature decreases since $\theta < \theta_1$.

We now turn to the theory of the present paper, which also admits constitutive assumptions of the form (6.13). Recalling the definitions for ψ', η', ϵ' given in §2, we write

$$\psi' = \psi \quad , \quad \eta' = c \log \theta \quad , \quad \epsilon' = c\theta \quad . \tag{6.18}$$

The inequality (4.4) is satisfied without imposing any restriction on α (or κ) and it is easily seen from (5.4) that again $\kappa \geqq 0$. For the present problem, with the use of (6.13) the condition (5.17) states that

$$\theta(t) > \theta_1 \quad \text{whenever} \quad c\theta - \alpha\dot{\theta} > c\theta_1 \tag{6.19}$$

for $t > t_1$. Using the same procedure as that which led to (6.17), we now obtain the result $\theta > \theta_1$ whenever (6.17) holds so that

$$0 > \alpha \quad . \tag{6.20}$$

This is in direct contradiction to the inequality $(6.14)_1$ demanded by the Clausius-Duhem inequality. Again, suppose that heat is supplied to the solid so that its temperature becomes $\theta(t) = \theta_1 + A(t-t_1)$. Then, from (5.17) and (6.13) we have

$$A > 0 \quad \text{whenever} \quad A[c(t-t_1) - \alpha] > 0 \tag{6.21}$$

for all $t > t_1$. In view of (6.20), the result (6.21) can only hold if $c > 0$. Furthermore, since $0 > \alpha$ and $\kappa \geqq 0$, wave propagation with a finite wave speed is possible and the waves are damped.

The above examples clearly demonstrate that the results obtained with the

use of the Clausius-Duhem inequality can sometimes be very different from those found by the procedure and ideas of the present paper. In the first example, the Clausius-Duhem inequality permits a perpetual motion of the second kind in the sense usually stated in books on thermodynamics. In the second example, the Clausius-Duhem inequality demands an undesirable restriction on the response of a rigid heat conductor and thus denies the possibility of propagation of heat as a wave with finite speed. Also, when the rigid conductor is subjected to a spatially homogeneous temperature field, the inequality requires that when heat is <u>supplied</u> to the conductor in a state of thermal equilibrium, the temperature of the conductor must <u>decrease</u>.

7. Basic jump conditions.

First we recall here the jump conditions which can be derived from the conservation laws for mass, linear momentum and moment of momentum. Consider a surface of discontinuity $\Sigma(t)$ in the present configuration of the body and let the normal velocity of a typical point of this surface be denoted by u. Then, assuming that the external body force $\underset{\sim}{b}$ is bounded on the surface Σ, the jump conditions which can be derived from the conservation laws mentioned above are

$$
\begin{aligned}
&[\![\rho \underset{\sim}{w} \cdot \underset{\sim}{\nu}]\!] = 0 \quad , \\
&[\![\rho \underset{\sim}{v} (\underset{\sim}{w} \cdot \underset{\sim}{\nu}) - \underset{\sim}{t}]\!] = 0 \quad .
\end{aligned}
\tag{7.1}
$$

In (7.1), $\underset{\sim}{\nu}$ is the unit normal to Σ chosen in a specified direction,

$$\underset{\sim}{w} = \underset{\sim}{v} - u\underset{\sim}{\nu} \tag{7.2}$$

and we have used the notation $[\![f]\!] = f_2 - f_1$, f_2 and f_1 being the values of f on either side of Σ. Similarly, assuming that both the body force $\underset{\sim}{b}$ and the external rate of supply of heat r are bounded on Σ, the jump condition at the surface of discontinuity Σ which can be derived from the conservation of energy (2.7) is

$$[\![(\tfrac{1}{2}\, \rho \underset{\sim}{v} \cdot \underset{\sim}{v} + \rho\varepsilon) \underset{\sim}{w} \cdot \underset{\sim}{\nu} - \underset{\sim}{t} \cdot \underset{\sim}{v} + h]\!] = 0 \quad . \tag{7.3}$$

The above well-known jump conditions $(7.1)_{1,2}$ and (7.3) at a surface of discontinuity are derived with the use of the transport theorem. To elaborate, let ϕ be any function per unit mass which takes different values ϕ_1 and ϕ_2 on either side of some surface of discontinuity in $\mathcal{P}$. Then (see Truesdell and Toupin 1960, Eq. (192.4)),

$$\frac{d}{dt}\int_{\mathcal{P}} \rho\phi \, dv = \int_{\mathcal{P}} \frac{\partial(\rho\phi)}{\partial t} dv + \int_{\partial\mathcal{P}} \rho\phi \, \underset{\sim}{v} \cdot \underset{\sim}{n} \, da - \int_{\sigma} [[\rho\phi]] \, u \, da \quad , \tag{7.4}$$

where the notations u and $[[\rho\phi]]$ have been introduced previously in (7.1) and (7.2) and where a part of the surface of discontinuity Σ is denoted by σ ($\subseteq \Sigma$) bounded by a closed curve $\partial\sigma$.

We now make use of (7.4) to obtain the jump condition from the entropy balance equation (2.3). It is convenient to consider a special region for $\mathcal{P}$ in the form of a cylinder but one which is still arbitrary. Let x^i ($i = 1,2,3$), be a set of convected coordinates and let the equation $x^3 = 0$ represent the surface of discontinuity Σ with position vector $\underset{\sim}{r} = \underset{\sim}{r}(x^1, x^2, t)$. Then, a point $\underset{\sim}{x}$ in the neighborhood of Σ may be represented as

$$\underset{\sim}{x} = \underset{\sim}{r}(x^1, x^2, t) + x^3 \underset{\sim}{\nu}(x^1, x^2, t) \quad . \tag{7.5}$$

For our present purpose, a part $\mathcal{P}$ of the body in the present configuration may be defined by surfaces $x^3 = \pm\alpha$ on each side of Σ and a surface $f(x^1, x^2, t) = 0$ which envelopes the part σ of Σ. Let $\partial\mathcal{P}_n$ refer to a part of $\partial\mathcal{P}$ specified by the cylindrical surface $f(x^1, x^2, t) = 0$ so that $\partial\mathcal{P}_n \cap \sigma = \partial\mathcal{P} \cap \sigma = \partial\sigma$ and let $\partial\mathcal{P}_n^c = \partial\mathcal{P} - \partial\mathcal{P}_n = \sigma' \cup \sigma''$, where σ' and σ'' refer to the surfaces $x^3 = \pm\alpha$, stand for the complement of $\partial\mathcal{P}_n$ in $\partial\mathcal{P}$. Then, using (7.4), application of (2.3) to the special region under consideration leads to

$$\int_{\sigma}\int_{-\alpha}^{\alpha}[[\frac{\partial}{\partial t}(\rho\eta) - \rho s - \rho\xi]]\,dx^3 da + \int_{\partial\sigma}\int_{-\alpha}^{\alpha}(\rho\eta\underset{\sim}{v}\cdot\underset{\sim}{n} + k)dx^3 ds$$

$$+ \int_{\sigma'}(\rho\eta\underset{\sim}{v}\cdot\underset{\sim}{n} + k)\Big|_{x^3=\alpha} da' + \int_{\sigma''}(\rho\eta\underset{\sim}{v}\cdot\underset{\sim}{n} + k)\Big|_{x^3=-\alpha} da''$$

$$- \int_{\sigma}[[\rho\eta]]\,u\,da = 0 \quad , \tag{7.6}$$

where da is an element of area of the surface σ, ds is the arclength on the boundary curve $\partial\sigma$ while da$'$ and da$''$ stand for the elements of area of the surfaces $x^3 = \alpha$ and $x^3 = -\alpha$, respectively. Within the region $\mathcal{P}$ under consideration, we assume that $\partial(\rho\eta)/\partial t$, k and the external supply of entropy ρs are finite but that the internal rate of production of entropy $\rho\xi$ may become unbounded on Σ. We assume that $\rho\xi$ is integrable and that†

$$\lim_{\alpha\to 0}\int_{-\alpha}^{\alpha}\rho\,\xi\,dx^3 = \rho\bar{\xi} \tag{7.7}$$

where $\bar{\xi}$ is a bounded function of x^1, x^2, t on Σ. Recalling that the normals to the surfaces $x^3 = \pm\alpha$ as $\alpha \to 0$ become $\pm\underset{\sim}{\nu}$, then from (7.6) in the limit as $\alpha \to 0$ we obtain

$$\int_{\sigma}\{[[\rho\eta\underset{\sim}{w}\cdot\underset{\sim}{\nu} + k]] - \rho\bar{\xi}\}da = 0 \tag{7.8}$$

for all arbitrary σ, where $\underset{\sim}{w}$ is defined by (7.2). With the usual continuity assumptions on Σ, we then obtain from (7.8) the jump condition

$$[[\rho\eta\underset{\sim}{w}\cdot\underset{\sim}{\nu} + k]] = \rho\bar{\xi} \quad . \tag{7.9}$$

It is possible to demonstrate the reason for an assumption of the form (7.7) for ξ in the special case of an elastic material. In the absence of a surface of discontinuity in $\mathcal{P}$, it is indicated in §3 that $\rho\xi\theta = -\underset{\sim}{p}\cdot\underset{\sim}{g}$ for an

† The volume integral in (7.6) contains both s and ξ, but only the latter field requires a constitutive equation which depends on the material. A motivation for the integrability of ξ in the form (7.7) is provided in the latter part of this section.

arbitrary elastic material. Suppose that the temperature distribution and its gradient in $\mathcal{P}$ are given by

$$\theta = (\theta_1+\theta_2)/2 - x^3(\theta_1-\theta_2)/2\alpha \quad , \quad \underset{\sim}{g} = -\underset{\sim}{\nu}(\theta_1-\theta_2)/2\alpha \quad , \tag{7.10}$$

where θ_1, θ_2 $(\theta_1 \neq \theta_2)$ are constants. If now $\alpha \to 0$, we have a surface of a discontinuity, say Σ, with a finite jump in θ across Σ but with $\underset{\sim}{g}$ becoming unbounded on this surface. However, since k (and hence $\underset{\sim}{p}$) in (2.4) is assumed to remain finite, it can be easily shown that the third term of the first integral in (7.6), namely

$$\int_\sigma \int_{-\alpha}^{\alpha} \rho\, \xi \, dx^3 da = \int_\sigma \int_{-\alpha}^{\alpha} \frac{\underset{\sim}{p} \cdot \underset{\sim}{\nu}(\theta_1-\theta_2)}{2\theta} \frac{dx^3}{\alpha} \quad , \tag{7.11}$$

tends to a finite limit as $\alpha \to 0$. This result clearly supplies a motivation for the more general assumption (7.7). In the case of an elastic material, an additional observation can be made regarding the limiting value $\bar{\xi}$. The function ξ in the integrand of (7.7) is always nonnegative, since for an elastic material $\rho\xi = -\underset{\sim}{p} \cdot \underset{\sim}{g}/\theta \geqq 0$ for any process. Hence the limiting value of the integral in (7.7) must also be nonnegative, i.e., $\rho\bar{\xi} \geqq 0$.

Before closing this appendix, we observe that since $\underset{\sim}{p}$ which depends on $\underset{\sim}{g}$ has been assumed to remain finite in the neighborhood of Σ, the conductivity tensor associated with $\underset{\sim}{p}$ must tend to zero in this neighborhood.

Acknowledgement. The work of one of us (P.M.N.) was supported by the U.S. Office of Naval Research under Contract N00014-75-C-0148, Project NR 064-436, with the University of California, Berkeley. Also, P.M.N. held a Senior Visiting Fellowship of the Science Research Council in the University of Oxford during 1975-76.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 14 UCB/AM-76-7	2. GOVT ACCESSION NO. 6	3. RECIPIENT'S CATALOG NUMBER 9
4. TITLE (and Subtitle) Supplement to Report AM-76-2 "On Thermodynamics and the Nature of the Second Law: I. Single Phase Continua. Supplement.		5. TYPE OF REPORT & PERIOD COVERED Technical Report.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 A. E. Green and P. M. Naghdi		8. CONTRACT OR GRANT NUMBER(s) 15 N00014-75-C-0148
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Mechanical Engineering, University of California, Berkeley, California 94720		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 064-436
11. CONTROLLING OFFICE NAME AND ADDRESS Structural Mechanics Program, Office of Naval Research, Arlington, VA 22217	11	12. REPORT DATE December 1976
		13. NUMBER OF PAGES 31
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 33p.		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Thermodynamics, the second law, balance of entropy, thermodynamic restrictions, jump conditions, two examples, some shortcomings of the Clausius-Duhem inequality.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The contents of this report supplement those of a previous report, namely Report No. AM-76-2, entitled "On thermodynamics and the nature of the second law: I. Single phase continua." In particular, the present supplement contains some additional development concerning the mathematical statement of the second law and restrictions on the heat conduction vector and internal energy, as well as two examples which demonstrate some shortcomings of the Clausius-Duhem inequality. One of the examples, (CONTINUED) next page

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S/N 0102-014-6601

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when studied with the use of the Clausius-Duhem inequality, leads to results that imply the possibility of a perpetual motion of the second kind. In the second example, which is concerned with a rigid heat conductor in thermal equilibrium, the Clausius-Duhem inequality requires that if heat is <u>added</u> to the medium the resulting spatially homogeneous temperature of the conductor <u>decreases</u>. Moreover, the inequality denies the possibility of propagation of heat in the conductor as a thermal wave with finite speed. The inequalities proposed here do not suffer from these shortcomings.